Novel Metal Perhydrides for Hydrogen Storage

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Project ID: STP 26

Overview

Timeline

- Start: April 1, 2004
- Finish: Phase 1, May 31, 2009;
  - total project, May 31, 2011
- % Complete: Phase 1, 50%

Budget

- Total Project funding
  - DOE – Phase 1: $694,816; total project: $1,719,806
  - Contractor – Phase 1: $195,677; total: $451,428
- Funding received in FY07: $250,000
- Funding received in FY08: $364,816

Barrier

➢ A. Cost
➢ B. Weight and Volume
➢ C. Efficiency

Partners

- Interactions/ collaborations
  - Clemson University
  - University of Minnesota
  - NanoMas, Inc.
- Project lead
  - Michigan Technological University

Objectives

- ## The overall focus of this project
  - Develop a new kind of materials that are able to bind hydrogen molecules into clusters
  - Enhance hydrogen adsorption/desorption by means of hydrogen cluster formation/decomposition so that the capacity of materials for hydrogen storage and the kinetics for hydrogen release have potential to meet the DOE 2010 and 2015 target

- ## The objective over the past year
  - Study the potentials and roles of charged/polarized species on hydrogen cluster formation
  - Examine the interaction behavior of charged species with hydrogen

- ## Relevance to Overall DOE Objectives
  - By the concept of charge-induced hydrogen cluster formation, the hydrogen storage capacity of the materials has potential to exceeding 0.06kg H_2/kg system, the DOE 2010 target

Milestones

12-01-2007:

- Material species with potential to form hydrogen clusters have been screened by computational approach

- Mechanisms for charged species to cluster hydrogen was revealed as a charge-transfer process

- Charge transfer between hydrogen and charged electrode was experimentally observed

- A bench scale reactor for experimentally investigation of hydrogen storage capacity of the new material system was built

12-01-2008 :

- The enhancement effects of applied potential on hydrogen adsorption will be identified

- Various electrode materials will be screened for optimized enhancement effect

- Effective electrode structures will be determined for maximum adsorption

- Suitable anode-cathode separation materials will be sought

Approach

- The study is focused on use of charged species to form H_2 clusters and thus to enhance the H_2 storage capacity
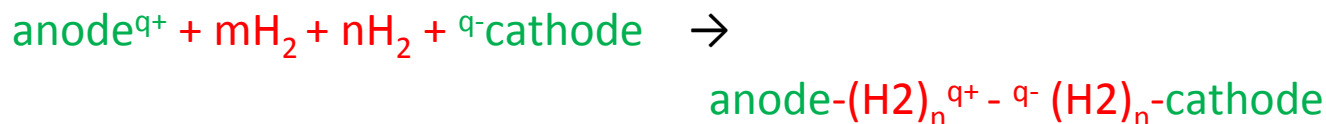
  – Proton-Hydrogen clusters:

  $$H^+ + nH_2 \rightarrow [H(H_2)_n]^+$$

  – Cation-hydrogen clusters:

  $$M^{Z+} + nH_2 \rightarrow [M(H_2)_n]^{Z+}$$

  – Anion-hydrogen clusters:

  $$X^{Z-} + nH_2 \rightarrow [X(H_2)_n]^{Z-}$$

  – Clustering H_2 around polar chemical bonds :

  $$mH_2 + {}^{\delta+}M\text{-}X^{\delta-} + nH_2 \rightarrow {}^{\delta+}[(H_2)_m M\text{-}X(H_2)_n]^{\delta-}$$

  – Clustering H_2 by charges on electrodes

  $$anode^{q+} + mH_2 + nH_2 + {}^{q-}cathode \rightarrow$$

  $$anode\text{-}(H2)_n{}^{q+} - {}^{q-}(H2)_n\text{-}cathode$$

Approach

- The study employed the following approaches
  - Computer modeling
    - Examine the potentials of cations, anions and polar chemical bonds for hydrogen cluster formation
    - Identify the cluster formation mechanism
    - Compare the cluster binding capabilities of different charged species
  - Experimental investigation
    - Create charges on electrodes

      electrodes + applied voltage $\rightarrow$ anode^{q+}— $^{q-}$cathode

    - Study interactions of hydrogen with charges on the electrodes by analyzing the changes of the anode potentials
    - If the charges on electrodes form bonds with H_2 molecules:

    anode^{q+} + mH_2 + nH_2 + $^{q-}$cathode $\rightarrow$ anode-$(H_2)_n^{q+}$ — $^{q-}$ $(H_2)_n$-cathode

      An anode potential change should be observed

Technical Progress/ Accomplishments Summary (I)

- Computer modeling
- The capability of cations for forming hydrogen clusters have been examined, including the ions of
  - alkaline metals
  - alkaline-earth metals
  - transition metals
- The capability of anions for forming hydrogen clusters have been examined, including O^{2-}, Cl^-, and C^-
- The capability of polar bonds in material compounds for forming hydrogen clusters have been examined, including
  - metal-oxygen bonds in alkaline-earth metal oxides and in transition metal oxides,
  - carbon-oxygen bonds in CO and CO2
  - H-Cl bond

- The capabilities of various charged species for forming hydrogen clusters were analyzed and compared based on
  - cluster formation energy
  - changes of bond length of H-H after and before cluster formation
  - bond length between hydrogen and the charged species
  - Charge transfer between hydrogen and the charged species
- The most promising charged species for forming hydrogen clusters have been selected, as summarized in the table below:

Charged Species	Hydrogen-Storage Capacity (wt.%)				
Cations	Be^{2+}	Mg^{2+}	Ca^{2+}		
	63.7	39.7	28.5		
Anions	O^{2-}	C^-	Cl^-		
	50	57.1	31.1		
Polar Bonds in Metal Oxides	Be-O	Cr-O	Fe-O	Co-O	Ni-O
	24.2	19	18.2	17.6	17.6

Technical Progress/ Accomplishments Summary (II)

- An dedicated instrument, namely electrode reactor, for examining the charge transfer between hydrogen and charged species has been developed

- Using electrode reactor, experimental investigations on charging/discharging behavior, with reflects the charge transfer between hydrogen and charged species, have been carried out

- Charge transfers between hydrogen and charges on anode were observed

- Data analysis indicates the charge transfer came from charge-induced hydrogen adsorption and desorption

- Some experiments on hydrogen sorption in materials containing charged species have been done with a volumetric sorption instrument, PCTpro-2000 (HyEnergy, Inc)

- Combination of the electrode reactor with the PCTpro-2000, is close to completion, which will be dedicated to study the hydrogen storage capacity of materials, in which charges can be concurrently generated by an external electric filed

Technical Progress/ accomplishments:

## Computer modeling: cation-hydrogen clusters
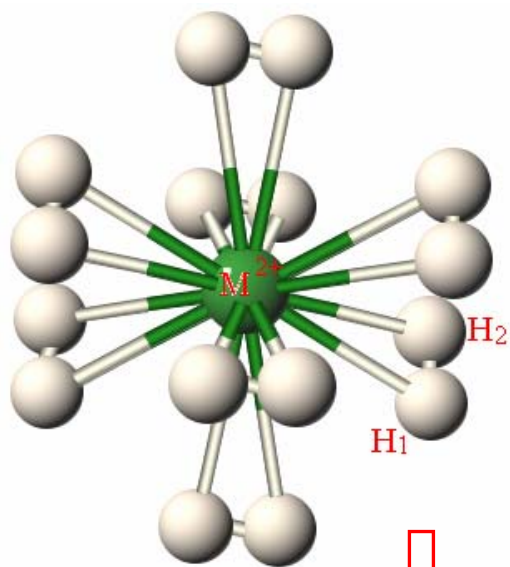
M^{2+} -8H_2 cluster core		Be^{2+}	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
Energy gain from 8H_2 + M^{2-} = M^{2+}-8H_2 (kcal/mole)		-154.99	-100.77	-63.35	-27.82	-20.82
Bond Length (Å)	M^{2+} -H1	2.109	2.324	2.596	3.225	3.488
	M^{2+} -H2	2.109	2.324	2.596	3.225	3.488
	H1-H2	0.755	0.755	0.753	0.747	0.743
Mulliken Charge	M^{2+}	-0.303	0.158	0.600	1.434	1.556
	H1	0.144	0.115	0.088	0.035	0.028
	H2	0.144	0.115	0.088	0.035	0.028

* Mulliken charge s: naked M^{2+}, +2; H in H_2, 0

- All cations show the capability to cluster hydrogen, but Be^{2+} , Mg^{2+} and Ca^{2+} are most promising
- Hydrogen-binding capacity: Be^{2+} , 63.7%; Mg^{2+} , 39.7%; Ca^{2+} , 28.5%
- The stability of the M^{2+}-H_2 clusters corresponds to changes of mulliken charges on M^{2+} and H_2 with and without the clusters
- Electron transfer from H_2 to M^{2+} is essential for formation of the clusters

# Technical Progress/ accomplishments:

Computer modeling: anion-hydrogen clusters
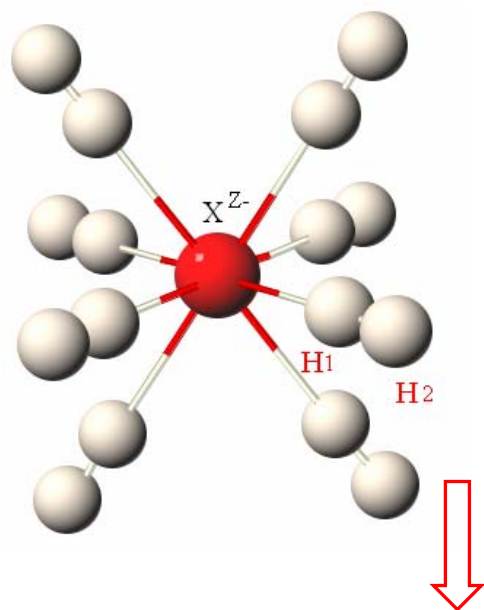
X^{Z-} -8H_2 cluster core		O^{2-}	Cl^-	C^-
Energy gain from $8H_2 + X^{Z-} = X^{Z-}$-8H_2 (kcal/mole)		-118.9	-14.6	--
Bond Length (Å)	X^{Z-}-H1	1.916	2.819	2.600
	X^{Z-}-H2	2.709	3.571	3.355
	H1-H2	0.793	0.751	0.755
Mulliken Charge	X^{Z-}	-0.776	-0.599	-0.606
	H1	0.259	0.040	0.048
	H2	-0.412	-0.090	-0.09

* Mulliken charge s: naked O^{2-}, -2; naked Cl^- and C^-; -1; H in H_2, 0

- Anions also show capabilities to bind H_2 molecules into clusters
- Hydrogen-binding capacity: O^{2-} , 50.0%; C^- , 57.1%; Cl^- , 31.1%
- Electron transfer from O^{2-} to H_2 is essential for formation of the clusters
- It is important for the oxygen anion to have the capability to bind H_2, because metal oxides are the most common polar bond materials
- It is also worthwhile to note the capability of C^- to form hydrogen clusters, since it can be made into a highly porous, lightweight electrodes

Technical Progress/ accomplishments:

Computer modeling: hydrogen clusters around M-O bond in alkaline-earth metal oxides
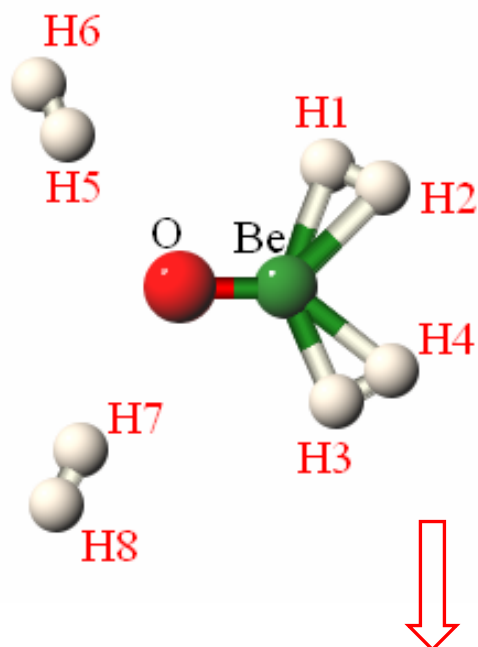
Energy gain from $4H_2 + BeO = BeO-4H_2$ (kcal/mole): -22.54					
Bond length between atoms in the cluster (Å)					
Be-O	Be-H1 Be-H3	Be-H2 Be-H4	H1-H2 H3-H4	O-H5 O-H7	O-H6 O-H8	H5-H6 H7-H8
1.338	1.612	1.743	0.768	2.401	3.145	0.749
Mulliken Charge at atoms in the cluster					
Be	O	H1, H3	H2, H4	H5, H7	H6, H8
0.171	-0.474	0.144	0.0212	0.0823	-0.0773

* Be-O without H_2: Bond length 1.332Å ; Mulliken charge Be, 0.386; O, -0.386

- Alkaline -earth metal oxides have polar M-O bonds as their structure units
- Among these metal oxides, BeO comes out as the most promising candidate
- Hydrogen binding capacity of Be-O: 24.2 H_2-wt.%
- Compare Be-O to Be^{2+}, it can be seen that the higher H_2-binding capacity of Be^{2+} is related to its larger amount of charge transfer

Technical Progress/ accomplishments:

Computer modeling: hydrogen clusters around M-O bond in transition metal oxides
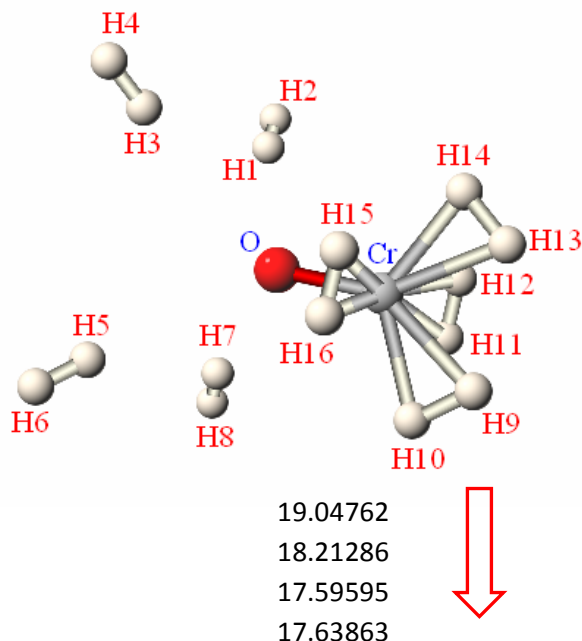
Energy gain from $8H_2 + CrO = CrO\text{-}8H_2$ (kcal/mole): -57.0

Bond length between atoms in the cluster (Å)

Cr-O	O-H1 O-H3 O-H5 O-H7	O-H2 O-H4 O-H6 O-H8	H1-H2 H3-H4 H5-H6 H7-H8	Cr-H9 Cr-H13	Cr-H10 Cr-H14	H9-H10 H13-H14	Cr-H11 Cr-H12 Cr-H15 Cr-H16	H11-H12 H15-H16
1.598	2.738	3.474	0.745	1.773	1.669	0.889	1.776	0.804

Mulliken Charge at atoms in the cluster

Cr	O	H1, H3, H5, H7	H2, H4, H6, H8	H9, H13,	H10, H14,	H11, H12, H15, H16
-0.118	-0.359	0.019	-0.027	0.451	0.069	0.070

* Cr-O without H_2: Bond length 1.553Å ; Mulliken charge Cr, 0.338; O, -0.338

19.04762
18.21286
17.59595
17.63863

- Calculations on transition metal oxides indicates the Cr-O, Fe-O, Ni-O, and Co-O bonds can also bind 8 H_2 molecules
- Hydrogen-binding capacity: Cr-O, 19.0%; Fe-O, 18.2%; Ni-O, 17.6%; Co-O, 17.6%
- Cluster formation free binding energies (kcal/mole): Cr-O, -57.0; NiO-8H_2, -34.6; CoO-8H_2, -20.8; FeO-8H_2, -20.7
- Compare Cr-O to Be-O, it can be seen that Cr-O involves with larger amount of charge transfer and has more negative cluster formation energy

Technical Progress/accomplishments:

## Experimental: hydrogen-material interaction in dc field
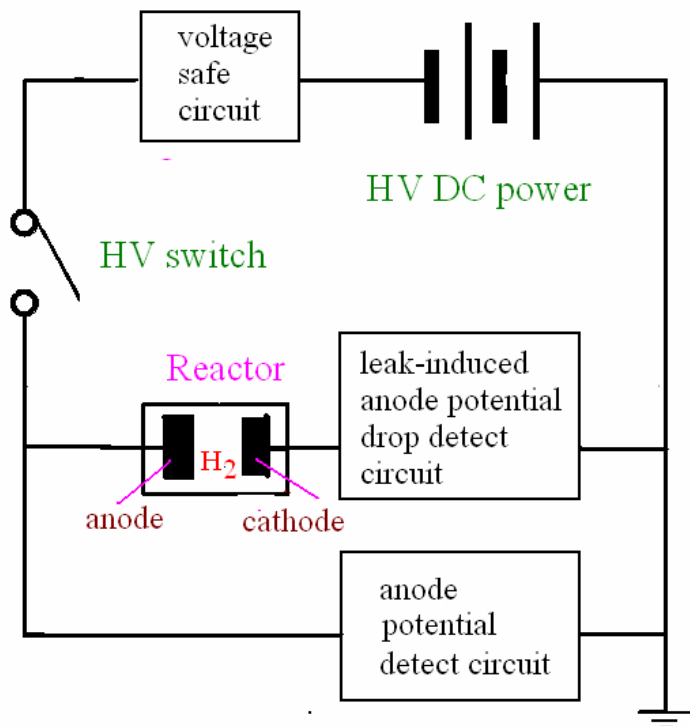
- With applied voltage, cations and anions can be created on the electrode surface, protons could also be generated
- Using dc-filed reactor is a convenient approach to investigate reaction behavior of hydrogen with charged species
- The instrument shown on the left has the function to examine charge transfer between hydrogen and electrodes. The charge transfer is anticipated to occur when hydrogen clusters form onto electrode surface
- The anode potential detect circuit measures the real-time potentials on the anode
- The leak-induced anode potential drop detect circuit measures the potential drop on the anode when charges flow from the anode onto the cathode
- The voltage safe circuit makes the cathode potential safe to personnel and equipment.
- Electrodes are made from electric conductive materials
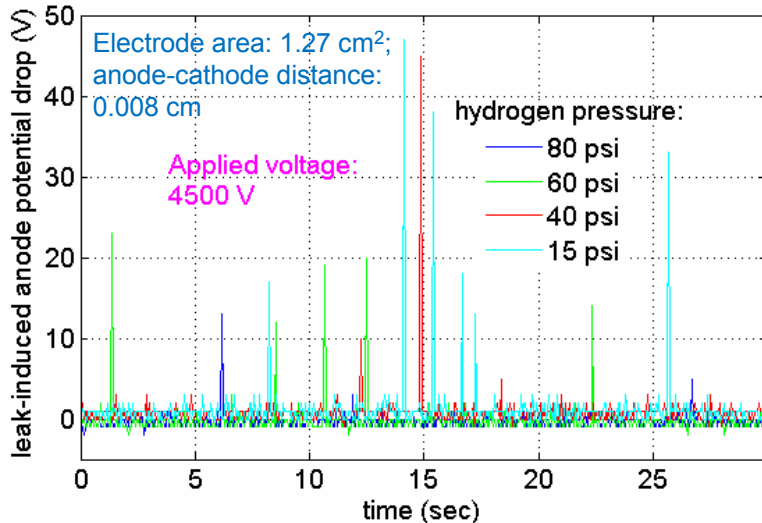- The HV switch is controlled by a computer program in order for data accuracy

Technical Progress/ accomplishments:

Experimental: hydrogen-material interaction in dc field during charge circle

Anode potential during charge circle under different hydrogen pressures
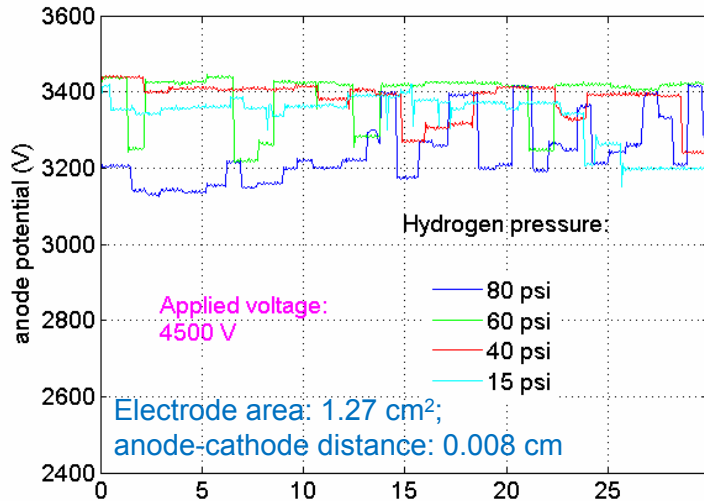

Anode potential drop caused by current leak between electrodes


- Experiments revealed significant anode potential fluctuations when a constant voltage is applied to the hydrogen filled electrode reactor (upper left figure)

- The drops of the anode potential caused by current leak between electrodes (lower left figure) are much smaller than the amplitude of the anode potential fluctuations (upper left figure)

- the anode potential fluctuation is attributed to charge transfer between hydrogen and the anode

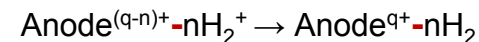- Charge-induced hydrogen adsorption/desorption on the anodes is possible:
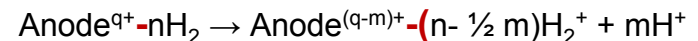
  1) H_2 adsorbed to the charged anode

     $iAnode^{q+} + nH_2 \rightarrow Anode^{q+}\text{-}nH_2$
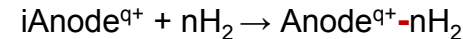
  2) electrons flow from the adsorbed H_2 to anode, anode potential drops

     $Anode^{q+}\text{-}nH_2 \rightarrow Anode^{(q-n)+}\text{-}nH_2^+$
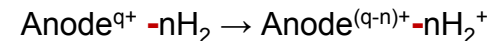
  3) Electrons from the anode flow back to the adsorbed H_2, anode potential rises

     $Anode^{(q-n)+}\text{-}nH_2^+ \rightarrow Anode^{q+}\text{-}nH_2$

  4) Some of the H_2 on the anode may be ionized, anode potential drops

     $Anode^{q+}\text{-}nH_2 \rightarrow Anode^{(q-m)+}\text{-}(n-\tfrac{1}{2}m)H_2^+ + mH^+$
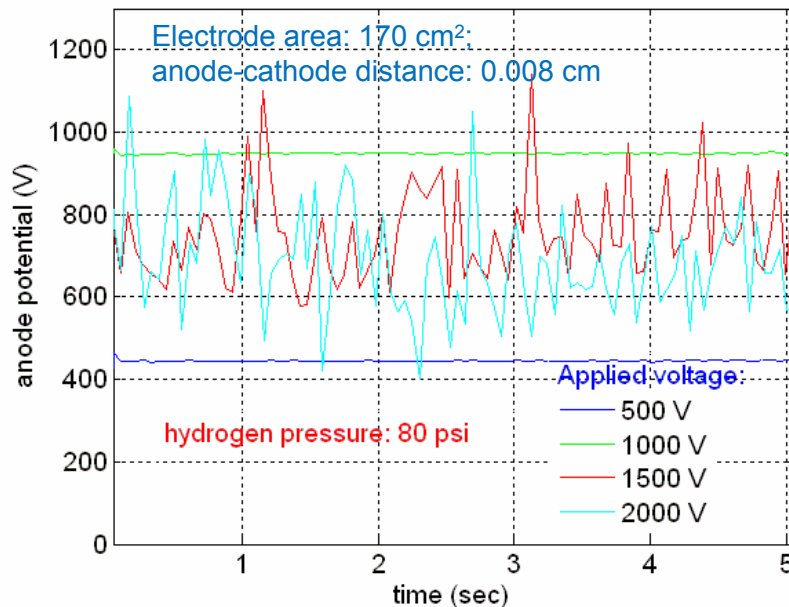
  5) If the protons reach the cathode and are neutralized, the corresponding signals should be observed as leak-induced anode potential drops (but the detected signals are insignificant, compare the lower figure to the upper figure)
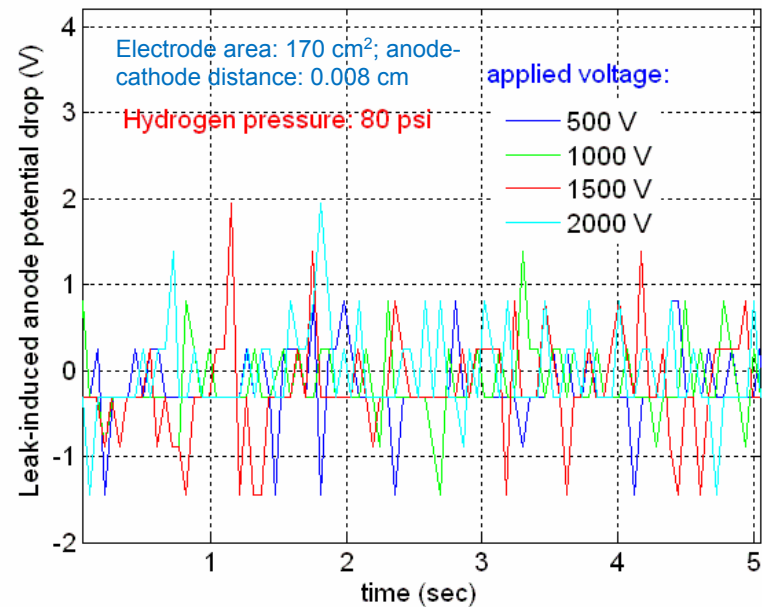
Technical Progress/ accomplishments:

Experimental: hydrogen-material interaction in dc field during charge circle

- With larger electrode area, the anode potential fluctuates at a lower voltage level (compare the upper figure Slide 13 and the left figure in this slide)
- Again the anode potential drop is not due to the current leak from the anode to the cathode (compare the two figures below)
- This phenomenon suggests that larger electrode area is more favorable to hydrogen-anode interaction

Anode potential during charging circle under various applied voltages

Electrode area: 170 cm^2; anode-cathode distance: 0.008 cm

hydrogen pressure: 80 psi

Applied voltage:
— 500 V
— 1000 V
— 1500 V
— 2000 V

Anode potential drop caused by current leak between electrodes

Electrode area: 170 cm^2; anode-cathode distance: 0.008 cm

Hydrogen pressure: 80 psi

applied voltage:
— 500 V
— 1000 V
— 1500 V
— 2000 V

Technical Progress/ accomplishments:

Experimental: hydrogen-material interaction in dc field during discharge circle
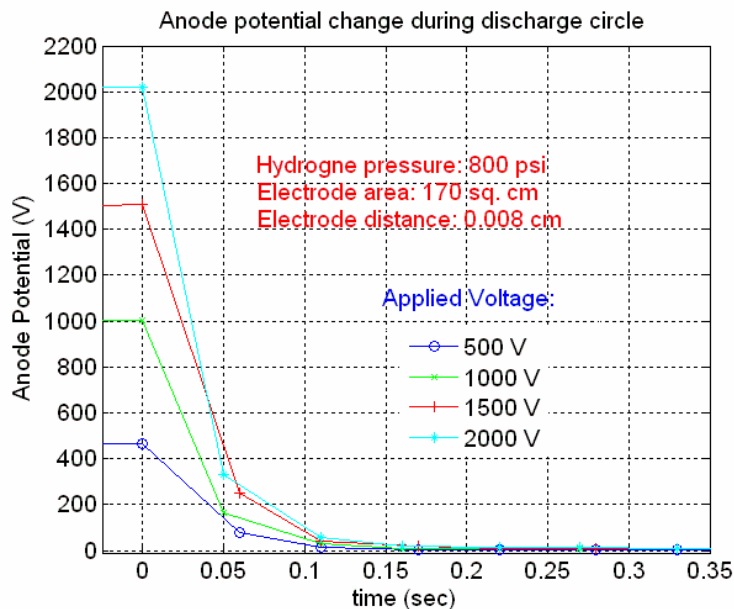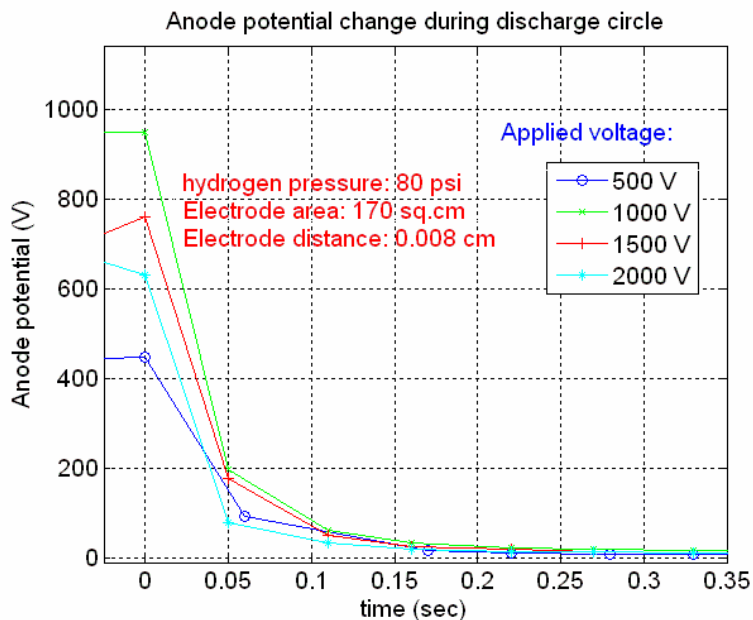
- Experimental data as shown in the figures revealed that the hydrogen filled electrode reactor behaves like a capacitor
- Without the hydrogen filled electrode reactor, the circuit lost this capacitor-like characteristics
- The phenomenon suggests possible release of hydrogen from the anode when the applied voltage is take off

$$Anode^{q+}\text{-}nH_2 \rightarrow Anode + nH_2 + qe^-$$

- The results from the two figures suggest that, under high voltages applied, higher hydrogen pressures may hold more hydrogen

Future work
FY08-FY09

- Investigate the effects of applied electric potential on hydrogen adsorption
  - Verify the charge-induced hydrogen adsorption/desorption process
    - Using a dedicated instrument that is able to measure hydrogen sorption in the hydrogen filled electrode reactor
  - Develop electrodes with large surface area and study the adsorption/desorption enhancement effect
    - Use mesoporous/nanoporous electrode materials
    - Use multilayer electrode structure
  - Further study the adsorption/desorption enhancement effects of applied voltage and hydrogen pressure, and explore the optimization approaches
  - Examine the adsorption/desorption enhancement effects of different electrode materials (starting from the metals explored by computer calculation), and screen the best candidates

Future work
FY08-FY09

- Investigate the hydrogen adsorption capability of materials with naturally polar bonds
  - Directed by our computer simulation, we will explore the following material compounds:

    BeO, Cr_2O_3, Fe_2O_3, NiO, and CoO
  - The experiment will be carried out with
    - Highly porous materials
    - Using these materials to modify the electronic structure of other materials
- Investigate the hydrogen adsorption capability of materials being electrically polarized, materials being explored will include
  - Inorganic ferromaterials
  - Organic ferromaterials
  - Other materials having charge carriers that can be electrically separa

Project Summary

- Relevance: By the concept of charge-induced hydrogen cluster formation, the hydrogen storage capacity of the materials has potential to exceeding 0.06kg H2/kg system, the DOE 2010 target

- Approach: Investigate charge-induced hydrogen cluster formation and develop materials systems that have charge-enhanced hydrogen adsorption/desorption

- Technical accomplishments and progress:

charged species	Hydrogen-storage capacity (wt.%)				
Cations	Be^{2+}	Mg^{2+}	Ca^{2+}		
	63.7	39.7	28.5		
anions	O^{2-}	C^-	Cl^-		
	50	57.1	31.1		
polar bonds in metal Oxides	Be-O	Cr-O	Fe-O	Co-O	Ni-O
	24.2	19	18.2	17.6	17.6

  - By computational screening a large number of various charged species, a number of most promising candidates were selected

  - Their high capacity for hydrogen storage (see Table) indicates that materials containing/consisting of these species have potentials to meet the DOE 2010 projective target

  - Experimental work observed of charge transfer between hydrogen and charged species, which indicates charge-induced hydrogen adsorption/desorption

- Proposed future research:

  - Verify the charge-induced H_2 sorption process using concurrent electric polarization and H_2 sorption reactor

  - Using Be, Mg, Ca as anode materials, examine the hydrogen storage capability

  - Develop new electrode structures in order to further enlarge the hydrogen storage capacity

  - Experimentally investigate the hydrogen storage capability of highly porous materials having Be-O, Cr-O, Fe-O, Co, Ni-O bonds

  - Experimentally investigate the hydrogen storage capability of materials having charge carriers that can be electrically polarized